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Incorporation of poly(glycidylmethacrylate) grafted bacterial cellulose nanowhiskers in poly(lactic acid) nanocomposites: Improved barrier and mechanical properties

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ABSTRACT

Poly(glycidyl methacrylate) (PGMA) was grafted onto bacterial cellulose nanowhiskers (BCNW) by means of a redox-initiated free radical copolymerization reaction. The incorporation of PGMA chains decreased the thermal stability and crystallinity of BCNW. The neat and the PGMA-grafted BCNW were subsequently incorporated as fillers into the PLA matrix. PGMA grafting improved both matrix-filler adhesion and the dispersion of cellulose nanocrystals. However, the dispersion of the nanofiller was still not completely optimized and loadings higher than 3 wt.% resulted in increased agglomeration. The incorporation of both neat and PGMA-grafted BCNW significantly reduced the oxygen permeability of PLA for low relative humidity conditions. However, due to the moisture sensitivity of cellulose, smaller improvements were attained when increasing the water activity. The detrimental effect of moisture on the oxygen permeability of nanocomposites was limited by the grafting copolymerization since PGMA-grafted BCNW seemed to present a more hydrophobic behavior. Furthermore, increased elastic modulus and tensile strength were observed for all the nanocomposites, especially when the concentration of nanocrystals was around the percolation threshold, i.e. 3 wt.%, but only nanocomposites containing PGMA-grafted BCNW preserved the ductility of neat PLA.

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1. Introduction

Currently, considerable research efforts have been focused on developing new plastic materials with low environmental impact. Biodegradable polymers and materials from renewable resources have attracted increased attention for sustainable development and environmental conservation. In particular, poly(lactic acid) (PLA) and polyhydroxyalkanoates (PHAs) are biodegradable and

bio-based materials with promising properties. PLA is an aliphatic polyester synthesized through lactic acid fermentation of natural feedstock such as corn or sugarcane [1,2] and it is one of the most widely used and well-studied bio-based polymers. It is highly transparent and rigid, with thermal and mechanical properties comparable to poly(ethylene terephthalate) (PET) [3]. However, its use has been limited because of its brittleness, low heat distortion temperature (softening above 60 °C) and relatively low barrier properties as compared to other packaging materials like PET. The incorporation of nanofillers such as nanoclays, carbon nanotubes and cellulose nanocrystals

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has been proven to be an efficient strategy for enhancing the properties of PLA and PLA-based hybrid materials [4–10].

Particularly, cellulose nanowhiskers (CNW) have generated a great deal of interest in the field of nanocomposites because they offer renewable and biodegradable character, high surface area, low density, and high mechanical strength [11]. Cellulose is mostly derived from plant sources, but it is also synthesized by some bacterial species, and bacterial cellulose nanowhiskers (BCNW) can be extracted by subjecting bacterial cellulose to an acid hydrolysis treatment [12]. These BCNW have a highly crystalline structure [12] and offer high aspect ratio [13,14]. The main drawback for CNW is their hydrophilic character, making them difficult to disperse in non-polar media. This may cause CNW to agglomerate in organic solvents and exhibit poor adhesion with hydrophobic matrices. Surface chemical modification by reaction of the hydroxyl groups present on the surface of cellulose nanocrystals with organomodifying agents has been proposed as one approach to overcome this shortcoming. In this regard, CNW have been successfully modified by acetylation [15–17], oxidation [18,19], silanization [20–22] and polymer grafting reactions [15,23–26] and incorporation of modified CNW into polymeric matrixes, such as PLA has also been reported [15,17,21,22,27].

Plant derived CNW were partially silanized and subsequently incorporated into PLA by solution casting, obtaining nanocomposites with an optimized nanofiller dispersion [21]. While the tensile strength and Young's modulus increased with the incorporation of silanized CNW, the elongation at break was reduced, suggesting that the matrix-filler adhesion did not improve. Similar results were observed for PLA nanocomposites incorporating acetylated CNW [27]. In a more recent study, silanized CNW were incorporated into a PLA matrix by melt compounding exhibiting a high level of nanofiller dispersion [22]. However, improvements on the tensile or barrier properties were not reported. In another study, PLA chains were grafted onto the surface of CNW by ring-opening polymerization and the subsequent incorporation into PLA by melt blending [15] indicated enhanced compatibility between the matrix and the nanofiller. No barrier or mechanical properties were reported for such material. Surface modification of CNW may be a viable option for enhancing their dispersion in organic solvents and to improve their compatibility with hydrophobic matrices, but further research is warranted to assess their impact on the mechanical and barrier properties of PLA.

In this study, the surface of BCNW was chemically modified by graft copolymerization of glycidyl methacrylate (GMA) using a redox-initiated free-radical method and modified BCNW were subsequently incorporated into PLA by solution casting. The epoxy group in the GMA chains was expected to react with the carboxylic group of PLA, thus promoting interfacial adhesion between BCNW and the polyester matrix. While cellulose modification by graft copolymerization of (GMA) has been reported [25,26], information on the incorporation of the grafted filler into polymeric matrixes is lacking. The morphology, thermal properties, oxygen barrier, water affinity and mechanical

properties of BCNW and BCNW-PGMA loaded PLA nanocomposites were investigated and compared to determine the influence of surface modification on the nanocomposites performance.

2. Materials and methods

2.1. Materials

Poly(lactic acid) (PLA) was a Polylactide Resin 4042D grade (Natureworks, LLC, Minnetonka, MN) with a weight average molecular weight (Mw) of ca. 6.6×10^4 g/mol. Glycidyl methacrylate (GMA) and ammonium cerium (IV) nitrate (CAN) were purchased from Aldrich (St. Louis, MO, USA). Sulfuric acid (96%) was purchased from Panreac (Barcelona, Spain). Nitric acid, methanol and acetone were supplied by Fisher Scientific (New Jersey, USA). Tetrahydrofuran (THF) and chloroform were purchased from Sigma-Aldrich (St. Louis, MO, USA).

2.2. Preparation of bacterial cellulose mats

Bacterial cellulose was obtained according to a published protocol [28]. Briefly, the bacterial cells (*Glucanacetobacter xylinus* 7351) were grown in a modified Hestrin/Shramm medium at 30 °C. The cells were pre-cultured in a test tube containing 5 mL of media and later transferred and scaled up to a larger reactor of 20 L at Bioinicia S.L., Valencia (Spain). The synthesized bacterial cellulose pellicles were sterilized and cleaned in boiling water followed by washing in a 10% (v/v) NaOH aqueous solution.

2.3. Preparation of bacterial cellulose nanowhiskers (BCNW)

At a neutral pH, bacterial cellulose (BC) pellicles were ground in a blender and the gel-like material was then compressed to remove most of the absorbed water. This material was then subjected to acid hydrolysis according to a previously optimized method [12]. BC was treated with a sulfuric acid solution (301 mL sulfuric acid/L water). About 7 g of BC was suspended in 1 L of sulfuric acid solution and it was heated and maintained at 50 °C with stirring for three days until a homogeneous solution was obtained. The cellulose nanowhiskers were recovered as a white precipitate after four centrifugation (12,500 rpm, 20 min) cycles in a Beckman Avanti J-25 centrifuge with a JA14 rotor. Recovered material was re-suspended in deionized water and neutralized with sodium hydroxide (7.0 pH) and centrifuged (12,500 rpm, 20 min) to obtain a partially hydrated precipitate which was stored at 4 °C or lyophilized for subsequent use. A portion of the material was solvent exchanged into acetone and chloroform. The water of the partially hydrated precipitate was replaced with acetone by applying several centrifugation cycles in which the supernatant was removed and replaced with acetone. After that, several centrifugation cycles were applied and acetone was replaced by chloroform. By means of this procedure BCNW were suspended into chloroform. The concentration of BCNW after chloroform evaporation was 48 wt.%.

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